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Fabrication of Metal Electrodes Based on the Self-Differentiation Technique Using the Novel High-and-Low Strategy

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Abstract. *In this study, a strategic analysis of the most successful printing techniques in terms of their capability to make high resolution patterns, i.e., the laser transfer and reverse offset printing techniques, is conducted and a novel self-differentiation technique is introduced on the basis of the modified strategy. The proposed self-differentiation technique is based on the high resolution subtractive patterning of a cheap material coated on a substrate and the subsequent low-resolution additive patterning of metallo-organic silver ink. The novelty of this self-differentiation technique lies in its capability to convert metallo-organic silver ink to either conductive or nonconductive patterns, as intended. With the proposed self-differentiation technique, conductive and nonconductive patterns were successfully self-differentiated, no matter where the metallo-organic silver ink was applied, and the line resistance of the self-patterned metal electrode, as fine as 190.1 ± 0.3 μm in line width, was as low as 24.8 ± 0.2 Ω/cm. © 2011 Society for Imaging Science and Technology.*
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INTRODUCTION

Printed electronics have attracted the attention of researchers for many years due to their inherent characteristics, including their process flexibility and low manufacturing cost. The fabrication of various kinds of electronic components such as radiofrequency antennas,[1] RC filters,[2] and thin film transistors (TFT)[3,4] has been successfully demonstrated with ink jet printing. Because of the pressure to further miniaturize electronic components, the fabrication of electrodes as small as a few tens of micrometers or less has long posed a problem, and researchers have concentrated their efforts upon the precise deposition and alignment of ink, as shown in Figure 1(a), with extremely small nozzles,[5,6] where a nozzle with a diameter of even less than 1 μm is used. Although direct ink jet printing is both the simplest form among all the other printing techniques and the ultimate goal to aim for, the adoption of such an extremely small nozzle not only raises a nozzle maintenance issue but also entails a great difficulty in providing such precise deposition and alignment. Moreover, the cost of an ink jet print head with extremely small nozzles must be significant because of the inevitably poor yield of ink jet print heads.

As an alternative route, the combinatorial process of ink jet printing with a surface energy patterning technique has been intensively explored,[7,8] as shown in Fig. 1(b), where low and high surface energy regions are prepatterned. Ink is repelled by the low-surface-energy-patterned regions and preferably resides in the high-surface-energy-patterned regions. Although this combinatorial process greatly improves the resolution and reliability, it needs an additional process such as photolithography to define the surface-energy-patterned regions. Moreover, the surface energy patterning technique has no capability to perfectly prevent the ink from spreading, so that short circuits are often formed when conducting ink crosses over the low-surface-energy-patterned regions.[9]

Therefore, a new approach requiring less effort for precise deposition and alignment has been requested. In addition, it is desirable to actively prevent the formation of short circuits when conducting ink is misplaced even between electrodes. In this study, the principal mechanism of the self-differentiation technique and the opportunity it provides for the fabrication of fine metal electrodes will be investigated.

In the section comprising the details of the experiment, the detailed experimental procedure will be described. In the former part of the Results and Discussion section, the morphological and electrical traits of the metal electrodes with the proposed self-differentiation technique will be investigated. For the implementation of the self-differentiation technique, a strategic analysis of the most successful printing techniques, i.e., the laser transfer and reverse offset printing techniques, will be conducted and the modified strategy with the self-differentiation technique, which inherits the merits but eliminates the demerits of the former printing techniques, will be discussed in the latter part of the Results and Discussion section. Finally, the conclusion will be presented in the Conclusion section.

DETAILS OF EXPERIMENT

Polyaniline (Panipol X, Panipol Ltd, Finland) was applied on glass microscope slides (Ref. 10 004 12, Paul Marienfeld, GmbH & Co. KG, Germany) with a spin coater (Spin 300A,

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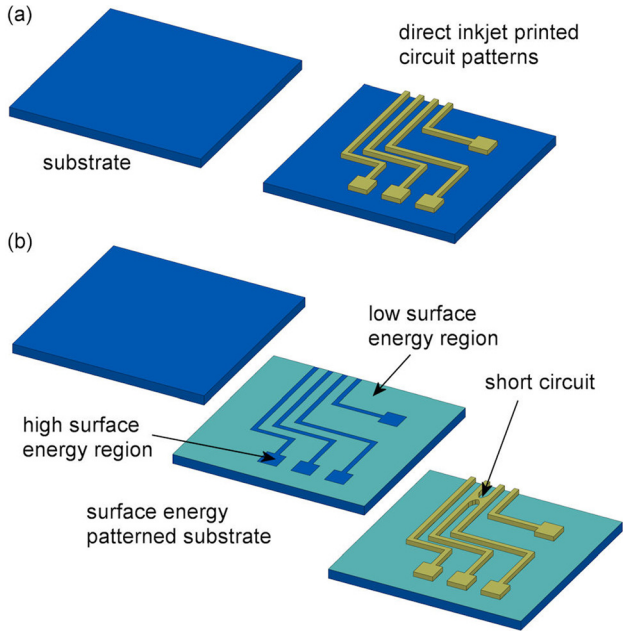

Figure 1. Metal electrode formation with ink jet printing: (a) direct ink jet printing and (b) with the surface-energy-patterning technique.

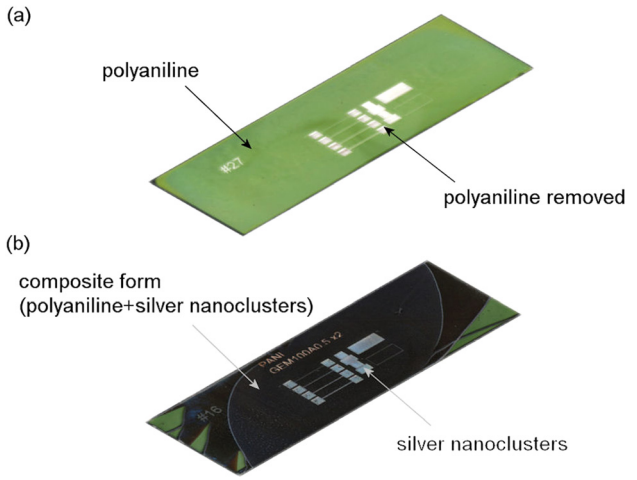

Figure 2. Sample preparation: (a) before and (b) after the deposition of metallo-organic silver.

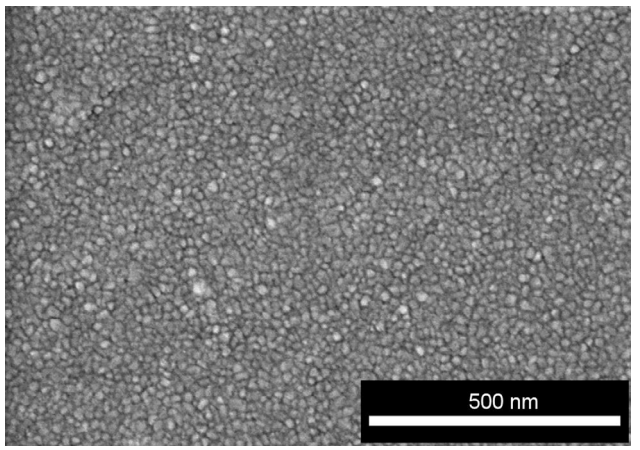

Figure 3. Morphology of the polyaniline layer composed of nanosized granules.

Midas System Co., Ltd, South Korea) at 1500 rpm for 30 s. After drying on a hot plate (GLHP-D3040, GlobalLab, South Korea), the polyaniline layer was selectively removed with a laser marker (U-5G, RMI Korea Co., South Korea). The driving current, marking step size, and frequency of the laser marker were set at 34.0 A, 5 μm, and 20 kHz, respectively.

As an adhesion promoter, (3-aminopropyl)trimethoxysilane (CAS 13822-56-5, Sigma-Aldrich Co., Mo) was added to the metallo-organic silver solution (C2080402D5, Gwent Electronic Materials Ltd., United Kingdom) at a concentration of approximately 2 wt. %. After the metallo-organic silver solution was spin-coated at 1500 rpm for 30 s on the laser-patterned sample, it was dried on a hot plate at 180°C for 5 min. To avoid unwanted pinhole defects, this procedure was repeated once more. The sintering of the sample at 230°C for 20 min converted the metallo-organic silver to a metallic state consisting of silver nanoclusters.

The electrical and morphological characteristics of the silver nanoclusters were measured with a four-point probe (Universal Probe, Jandel Engineering, Ltd, United Kingdom) and a source-meter (Model 2400, Keithley Instruments, Inc.), and a field emission scanning microscope (Nova NanoSEM 230, FEI Company, Ore), respectively.

RESULTS AND DISCUSSION

This section commences with an investigation of the experimental results, followed by a strategic analysis of the previous printing techniques. In accordance with the result of the strategic analysis, a new strategy that incorporates the proposed self-differentiation technique will be proposed.

Experimental Results of Self-Differentiated Metal Electrodes

The laser-patterned polyaniline sample before the deposition of the metallo-organic silver solution is shown in Figure 2(a), and the sintered polyaniline sample after the deposition of the metallo-organic silver solution is shown in Fig. 2(b).

Polyaniline has three different oxidation states, i.e., pernigraniline, emeraldine, and leucoemeraldine,[10,11] but only the emeraldine form of polyaniline is conductive. In this study, the emeraldine form of polyaniline, the color of which is green, was used. As shown in Figure 3, the dried polyaniline layer is composed of nanosized granules, the average size of which is less than 50 nm, and it has the capability to absorb metallo-organic silver solution through the voids between the granules.

The positive charge of the polyaniline in the emeraldine form is stabilized with dodecyl benzene sulfonic acid. When the metallo-organic silver solution permeates into the polyaniline layer, the oxidation state of the polyaniline changes due to the negatively charged carboxyl group of

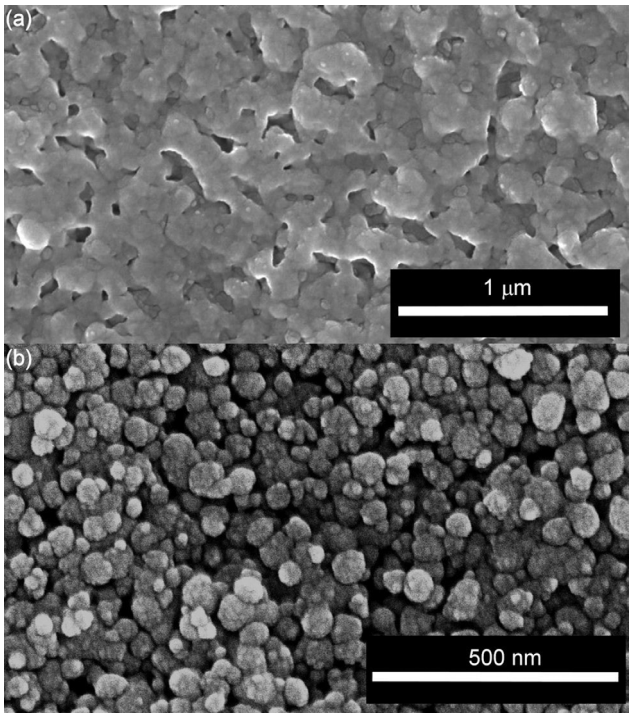

Figure 4. Fusion status of silver nanoclusters: (a) with and (b) without (3-aminopropyl) trimethoxysilane.

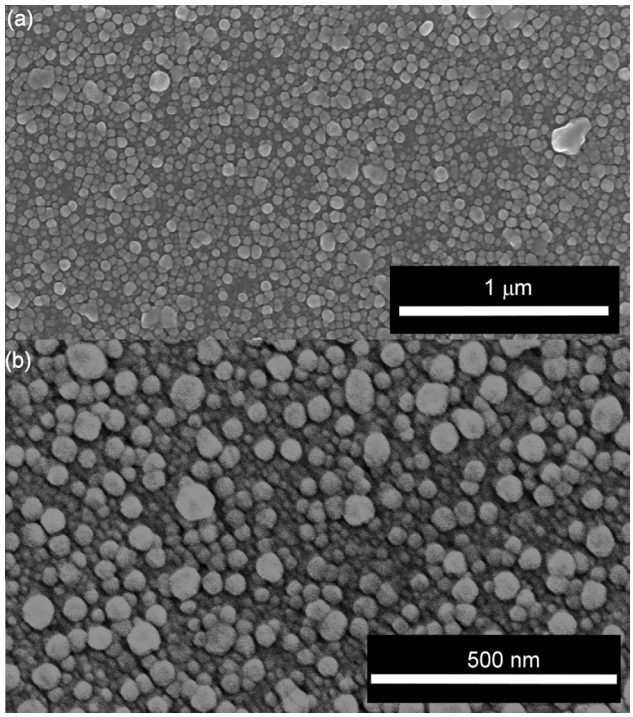

Figure 5. Isolated silver nanoclusters due to the presence of polyaniline: (a) with and (b) without (3-aminopropyl) trimethoxysilane.

metallo-organic silver: as a result, the emeraldine form of the polyaniline becomes the nonconductive pernigraniline form and its color changes from green to black, as shown in Fig. 2(b). This chemical reaction is one source of the conductivity loss of the polyaniline, another source being the thermal degradation that occurs during the sintering process of the metallo-organic silver at temperatures as high as 230°C.[12,13]

During the sintering process, the organic species of metallo-organic silver are burnt away[14,15] and silver nanoclusters are formed from silver atoms in the carboxyl group of the metallo-organic silver. Figure 4(a) shows the morphology of the silver nanoclusters, which are found to fuse well with each other. The best measured sheet resistance is around $1.70 \pm 0.09\ \Omega/\square$.

On the other hand, if the metallo-organic silver is deposited on the polyaniline layer and sintered, the formed silver nanoclusters are prevented from fusing with each other and hence they remain isolated, as shown in Figure 5(a). The measured sheet resistance is around $11.2 \pm 6.7\ G\Omega/\square$, and this composite, consisting of polyaniline and isolated silver nanoclusters, could be considered as an insulator.

It is clearly seen that the addition of (3-aminopropyl) trimethoxysilane greatly enhances the fusion status of the silver nanoclusters, when compared to that without (3-aminopropyl)trimethoxysilane, as can be seen in Fig. 4. However, the addition of (3-aminopropyl)trimethoxysilane shows no distinct influence on the isolation status of the silver nanoclusters, as shown in Fig. 5. If the addition of (3-aminopropyl)trimethoxysilane is optimized, the conductivity contrast of the silver nanoclusters in the region from which polyaniline has been removed, as can be seen in Fig. 4(a), and the region with polyaniline, as can be seen in Fig. 5(a), might become even higher due to the improved fusion status of the silver nanoclusters, compared to Figs. 4(b) and 5(b). However, the addition of extra chemical compounds above a certain amount generally decreases the conductivity of the silver nanoclusters after sintering, although it might improve the fusion status of the silver nanoclusters as well as the adhesion and mechanical properties of the sintered part. Because the optimization of additives is not the scope of this study, it is left for further investigation in the future.

The insulating characteristics of the composites were measured with two adjacent electrical pads. When these pads were kept apart at distances of 10.1 ± 0.8, 27.2 ± 0.4, and $50.1 \pm 0.4\ \mu$m, the measured electrical resistance values were 0.03 ± 0.0, 519.8 ± 45.9, and $1090 \pm 35.4\ M\Omega$, respectively. The line resistance was characterized with a digital multimeter (Model 189, Fluke Corp., WA), and the measured line resistance values were 78.9 ± 1.8, 38.3 ± 0.4, and $24.8 \pm 0.2\ \Omega/cm$ when the electrode widths were 95.6 ± 0.7, 136.7 ± 0.9, and $190.1 \pm 0.3\ \mu$m, respectively. The characterized insulation and line resistance values are summarized in Tables I and II.

As discussed above, the "to-be-conductive" region becomes conductive and the "to-be-nonconductive" region becomes nonconductive, no matter where metallo-organic silver is present, because the presence of polyaniline eventually controls the conductivity of the silver nanoclusters via their controlled fusion and isolation. This ability to differentiate conductive and nonconductive patterns is the most unique feature of the proposed technique, distinguishing it

Table I. Measured insulating characteristics with varying pad-to-pad distances.

Pad-to-pad distance (μm)	Resistance (MΩ)
10.1 ± 0.8	0.03 ± 0.0
27.2 ± 0.4	519.8 ± 45.9
50.1 ± 0.4	1090 ± 35.4

Table II. Measured line resistance with varying electrode widths.

Electrode width (μm)	Unit resistance (Ω/cm)
95.6 ± 0.7	78.9 ± 1.8
136.7 ± 0.9	38.3 ± 0.4
190.1 ± 0.3	24.8 ± 0.2

from previous printing techniques and has, thus, been named the "self-differentiation technique."

Before pursuing further discussion on the way to implement this self-differentiation technique, the most successful printing techniques to date will be analyzed in the Strategic Analysis of Previous Printing Techniques section and their demerits discussed.

Strategic Analysis of Previous Printing Techniques

As of now, two printing techniques have shown the most successful results in terms of their high resolution and large area patterning capabilities. The first one is based on a laser technology[16–18] and the other on a relief plate, called "cliché."[19–21]

As can be seen in Figure 6, the laser transfer technique utilizes a donor film onto which a functional material is coated. The donor film is placed on a substrate and then laser scanning is carried out to transfer a functional material to the substrate. After the laser scanning, the donor film is removed and a substrate with transferred patterns is obtained. Because the pattern resolution is basically proportional to the size of the laser beam spot, it has an inherently high resolution patterning capability.

However, this laser transfer technique is sensitive to the laser power fluctuations and surface energy states of the donor film and substrate. For the construction of a donor film, the adhesion of a functional material to the donor film and substrate as well as the cohesion of a functional material must be carefully controlled, which makes the employment of the laser transfer technique difficult.

On the other hand, the reverse offset printing technique is based on the interaction between blanket, ink, and relief plate, called cliché, as shown in Figure 7. First, ink is coated on a blanket made of a kind of silicon rubber. While the ink-coated blanket is in contact with a cliché, ink is transferred from the blanket to the raised part of the cliché. The remaining ink on the blanket is eventually transferred to a substrate.

The pattern quality of the reverse offset printing technique is excellent and almost comparable to that of photolithography. The high resolution capability of the reverse offset printing technique is also superb, and the minimum line width and gap are as small as 10 and 6 μm, respectively.[19] Now, the reverse offset printing technique is known to continuously print out patterns on 6000 sheets of glass in the fifth-generation size of the TFT LCD industry.

In accordance with the strategic analysis, both techniques are found commonly based on the high-and-low strategy, as can be seen in Figure 8(a). The ink coating on either donor film or blanket is considered as the low strategy, but the selective removal with either laser or cliché is considered as the high strategy in terms of resolution. Both of them are successful because they do not seek high resolution patterning with an additive process. The additive process is only used for the preparation of the donor film or the ink-coated blanket at low resolution, and high

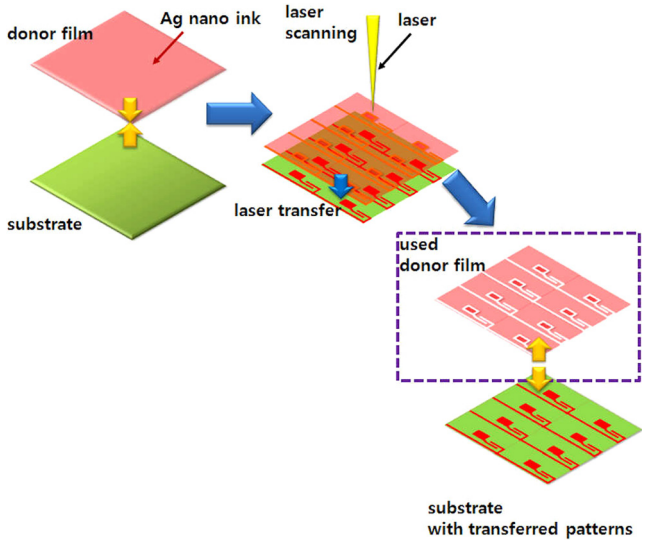

Figure 6. Process steps of the laser transfer technique.

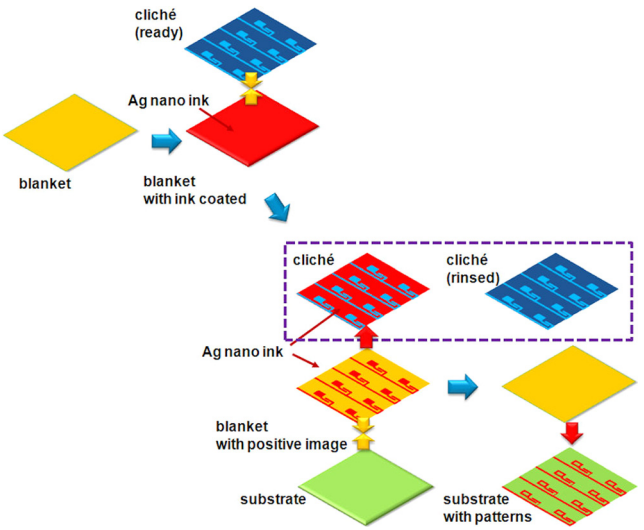

Figure 7. Process steps of the reverse offset printing technique.

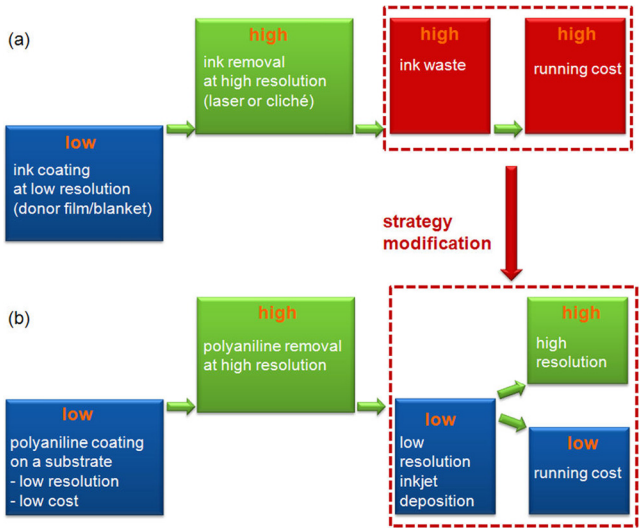

Figure 8. Strategic analysis of (a) the laser transfer and reverse offset printing techniques and (b) the self-differentiation mechanism.

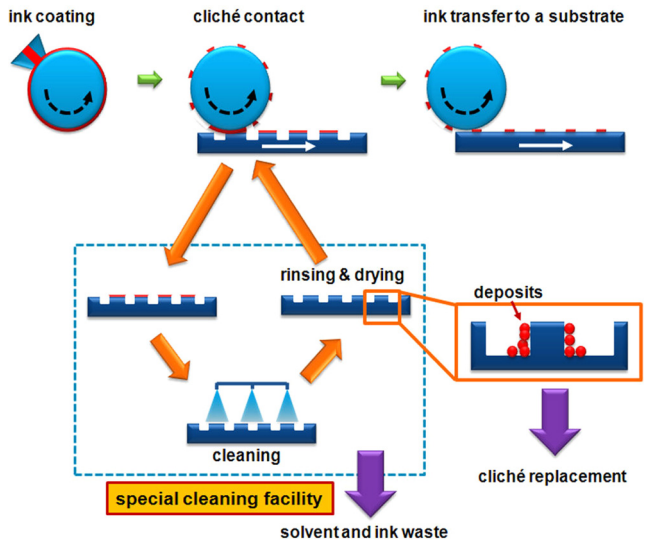

Figure 9. Cleaning of the used cliché after each printing run in the reverse offset printing technique.

resolution patterning is accomplished by a selective subtractive process with laser or cliché.

Although this strategic approach is successful in producing high resolution patterns, the consumption of material is very high because the remaining functional material on either the donor film or the ink-coated blanket is mostly wasted. When we consider the fabrication of metal electrodes in a TFT LCD backplane with silver nano ink as an example, it is found that the TFT LCD backplane has a blank space of more than 85% because the TFT LCD display basically operates in a transmissive mode. This implies that only 15% of the silver nano ink is transferred to a substrate, while the rest of the silver nano ink will be discarded in the case of the donor film or rinsed away in the case of the cliché.

Especially, the cliché of the reverse offset printing technique needs to be cleaned after each printing run to remove any functional material from the raised part of the cliché. Therefore, a special cleaning facility is required and a massive amount of solvent is consumed for this cleaning purpose, as can be seen in Figure 9.

During the cleaning of the used cliché, another cliché must be loaded for continuous production and this implies that a set of multiple clichés is required, further increasing the operating cost. In addition, the nature of the contact printing between functional material and cliché tends to increase the possibility of unwanted deposits around the engraved corner of the cliché. This shortens the lifetime of a cliché and contributes to the increase of the operating cost for the replacement of clichés.

When ink is coated on a blanket, a part of the solvent is absorbed into the blanket. This solvent absorption eventually changes the properties of the silicon rubber and contributes to a critical dimension change in the patterned line width.[22] As a result, the used blanket needs to be regularly dried and finally replaced, which also contributes to an increase in the operating cost.

Strategic Modification with the Self-Differentiation Technique

Given the aforementioned issues concerning the waste of precious functional material, the operating cost of the blanket/cliché/cleaning facility, and the critical dimension change of the printed line width caused by solvent absorption in the blanket, the high-and-low strategy of the laser transfer and reverse offset printing techniques needs to be modified.

To save a precious functional material—in this case metallo-organic silver for the fabrication of metal electrodes, it should be selectively deposited with an economic means such as ink jet printing instead of coating. This selective deposition of an expensive material significantly contributes to a reduction of costs, compared to the laser transfer and reverse offset printing techniques. However, the resolution of ink jet printing is limited so that a laser is chosen as another noncontact-based means, capable of producing high resolution patterns.

The resolution mismatch between ink jet and laser is compensated with polyaniline. As shown in Fig. 8(b), the low-cost material, polyaniline, is coated at low resolution on a substrate. The selective removal of the polyaniline at high resolution is performed with a laser. The postprocess, such as sintering, subsequent to ink jet deposition at low resolution, eventually turns the deposited metallo-organic silver into silver nanoclusters so that highly conductive metal electrodes are achieved where the polyaniline has been removed with the laser. These process steps are summarized in Figure 10.

However, this modified high-and-low strategy would fail if the silver nanoclusters formed from the metallo-organic silver were to build an electrically conductive network between metal electrodes. Here, the self-differentiation technique, which is used to differentiate conductive and nonconductive regions by controlling the fusion and isolation of

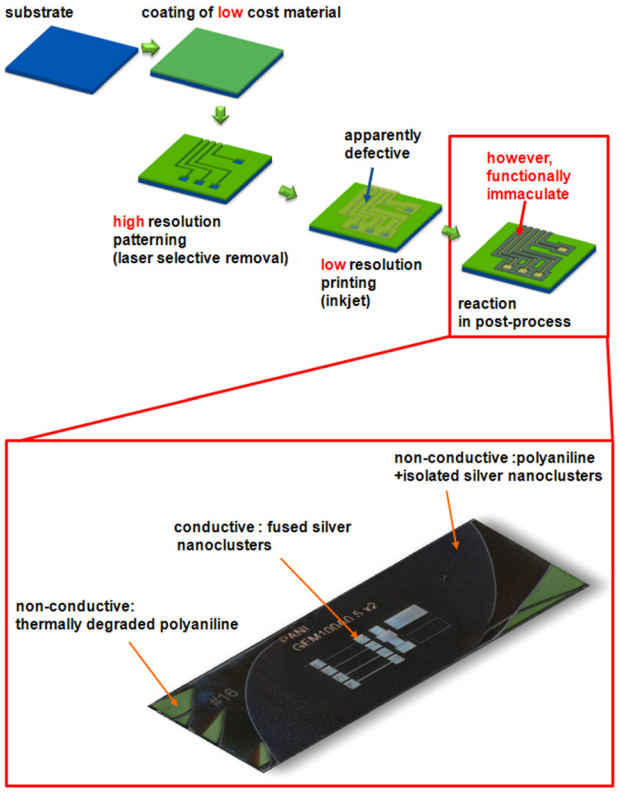

Figure 10. Process steps of the modified high-and-low strategy with the self-differentiation mechanism.

silver nanoclusters, helps the successful implementation of the modified high-and-low strategy. Due to the presence of polyaniline, which inhibits the final conductivity, the silver nanoclusters are prevented from fusing with each other so that the intended "to-be-nonconductive" regions between the metal electrodes remain nonconductive.

CONCLUSION

In this study, a novel self-differentiation technique is proposed and its fundamental mechanism is investigated. After laser patterning the polyaniline layer, which is composed of sub-50 nm nanosized granules, the metallo-organic silver is deposited and then sintered at 230°C for 20 min. This thermal process converts the metallo-organic silver into a metallic state of silver nanoclusters. In the absence of polyaniline, silver nanoclusters are found to fuse well with each other and their best sheet resistance is as low as $1.70 \pm 0.09\ \Omega/\square$. On the other hand, the fusion of silver nanoclusters is found to be inhibited by the polyaniline, and the sheet resistance of the composite, i.e., polyaniline and isolated silver nanoclusters, is as high as around $11.2 \pm 6.7\ G\Omega/\square$.

This self-differentiation mechanism is incorporated with the modified high-and-low strategy to produce metal electrodes. The modified high-and-low strategy is composed of (1) a relatively easy step involving the removal of polyaniline to prepare fine electrode regions at high resolution with a laser and (2) a step involving the rough deposition of metallo-organic silver solution at low resolution and successfully self-differentiates conductive and nonconductive patterns.

Unlike conventional approaches, efforts to deposit conductive ink precisely can be eliminated with this self-differentiation technique. Compared to the previous printing techniques, such as laser transfer and reverse offset printing, it is found to be more effective in terms of the reduced consumption of an expensive material. In addition, this self-differentiation technique provides an active means to prevent the formation of short circuits.

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